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THERMAL AGING OF SILVER-PLAIED COPPER AIRCRAFT ELECTRICAL WIRE

AIR FORCE MATERIALS LABORATORY

MAY 1973

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THERMAL AGING OF SILVER-PLATED COPPER AIRCRAFT ELECTRICAL WIRE

L. R. BIDWELL

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L. R. BIDWELL

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FOREWORD

This program was conducted under Project 7351, "Metallic Materials for Air Force Weapon System Components" during the periods August 1971 - January 1972 and November 1972 - January 1973.

The investigation was performed in the Metals and Processing Branch of the Metals and Ceramics Division, AFML, Wright-Patterson Air Force Base, Ohio 45433. The able assistance of Messrs. Gary Teeters, Russell Pence, and William Hillan of Monsanto Chemical Corp., Marlin Cook of the University of Cincinnati, and James Soloman of the University of Dayton in various phases of the experimental work is gratefully acknowledged.

This report was released for publication in April 1973.

This technical report has been reviewed and approved.

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ABSTRACT

FEP/polyimide-insulated silver-plated copper aircraft electrical wire was thermally aged at temperatures of 150°-230°C for periods of up to 1000 hrs. The wires were examined for evidence that the insulation contributed to strand blocking during high temperature exposure. No evidence for a reaction between the insulation and the metal conductors was found. The phenomenon can be attributed entirely to the interstrand diffusion of silver. Two types of conductor degradation, unrelated to strand blocking, were identified. The nature, possible cause, and probable effect of each is discussed and a change in the current temperature rating procedure is recommended.

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I. INTRODUCTION

In the past, the maximum use temperature of most of the common types of coated aircraft electrical transmission wire has been limited by the properties of the insulating material. With the introduction of new, more heat-resistant materials, such as Teflon and FEP-fluorocarbon-coated polyimide films, it has been possible to substantially increase the temperature rating of such wire. This has been a desirable trend for applications in high-performance military aircraft. The potential heat load encountered has been significantly increased both by the use of smaller wire sizes in order to conserve weight and by the higher ambient temperatures resulting from aerodynamic heating.

Prior to the last three years the adequacy of the conductor material at higher operating temperatures had been largely taken for granted. In response to the increasing concern expressed by aircraft designers, McCune of the Hudson Wire Co. and Burns, Busch, and Larson of the Grumman Aerospace Corp.[1] conducted a joint evaluation of the degradation in electrical conductivity, flex life and solderability of tin, silver, and nickel-plated wire exposed to normal service temperatures. These investigators identified a number of potential problem areas which heightened concern within the wire and aircraft industries, instigating a flurry of further wire aging investigations.

One of the more noticeable phenomena encountered in these studies was a marked decrease in the apparent flexibility of polyimide-insulated unidirectionally stranded (unilay) silver-plated copper (SPC) wire as compared to concentrically stranded material. This effect was presumed to be due to a greater degree of strand blocking (fusion or welding of individual wire strands). In unilay constructed wire, successive strand layers are wound around a central core strand in the same direction, whereas in concentric construction the layers are wound in alternate directions. Unilay wire is relatively new and is favored by some aircraft manufacturers in the design of new high-performance aircraft because of increasingly severe space restrictions. For a given conductor cross section, unilay wire occupies less space than the concentric wire and, furthermore, can be manufactured to closer tolerances because of the closer strand packing. Both of these features are further enchanced by drawing the stranded wire through a die. While one would expect considerably greater longitudinal interstrand contact area in unilay wire as compared to concentric construction (the line contact of nestled strands vs. the point contact of crossed strands) and thus a greater tendency for strand blocking due to the interdiffusion of silver during elevated temperature exposure, the loss of flexibility and potential wire degradation experienced in the aging studies was much more pronounced than anticipated. The possibility that a detrimental reaction between the conductors and the polyimide insulation might be a contributing factor was of

considerable concern to the Criteria, Antenna, and Radomes Branch of the ASD Directorate of Avionics Subsystems Engineering and it was in response to their request that the present metallurgical analysis of thermally aged, polyimide-insulated, unilay SPC wire was initiated.

II. EXPERIMENTAL PROCEDURE

A. Material

The above request suggested an examination of MIL-W-81381/7, No. 20 (19/32) wire given an accelerated aging treatment of 500 hrs. at 230°C. This type of wire contains 19 strands of 8 mil, unidirectionally wound, silver-plated copper wire. It is insulated with two wrappings of 1 mil polyimide tape coated on both sides with 0.1 mil of FEP-fluorocarbon resin. Each wrapping is overlapped a minimum of 50%. The wire is finished with an outer covering of 1 mil modified aromatic polyimide resin. A typical cross-sectional view is shown in Fig. 1a. MIL-W-81381/7 wire is rated for continuous, indefinite, use at 200°C, and the suggested exposure of 500 hrs. at 230°C corresponds to the life cycle exposure test established by the military specification.

For comparative purposes, it was recommended that a similar study be conducted on concentric stranded MIL-W-22759/11 Teflon-insulated wire. This type of wire is covered with a single, monolithic, extruded, coating of Teflon. The wire supplied was No. 18 (19/30), which is constructed from 19 strands of nominally 10 mil SPC conductor (see Fig. 1b).

B. Aging Procedure

The initial wire samples were thermally aged in an electrically operated free airflow oven controlled to $\pm 2^{o}C$. A series of 1 ft and 4 ft sections of wire were aged simultaneously, with samples being withdrawn at the end of 125, 264, and 500 hr. periods, in order to qualitatively establish the kinetics of any reaction that might be observed. A rather curious, initially unexplainable, deterioration was noted in the silver plating at the end of these tests; consequently, additional aging treatments were conducted at 150^{o} and $200^{o}C$ for periods up to 1000 hrs. For these tests, a second oven with a forced-air circulating system, and the same temperature control capability, was utilized also.

At the end of the aging treatments specimens were taken from the wire samples at the ends and from the centers of both the 1 ft and 4 ft sections. All samples were examined metallographically and selected ones were further examined by scanning electron microscopy and electron microprobe analysis.

For reasons which will be discussed later, several series of aging treatments were conducted on wires with the insulation removed. Insulation removal was accomplished by abraiding one side down to the silver plating, permitting the remainder of the insulation to be peelod off. This method confined the damage to the silver plating to a few strands, leaving the major portion of the wire undamaged. In order to avoid contamination of the silver plating and to facilitate handling, the insulation was left intact on one end of tho wire. During aging, the

wires were placed in new pyrex beakers to prevent contact with the oven lining.

C. Metallography

The metallographic studies were conducted on transverse sections of wire. Each wire section, with the insulation intact, was placed in a small block of cured phenolic resin, to aid in edge retention, and then infiltrated with an epoxy cement to hold it in place and to minimize the amount of polishing debris that could be trapped within strand interstices. The phenolic block was then mounted in a standard lucite metallographic mount. The samples were ground through 600 grit silicon carbide papers, finishing with a fine grinding on 4/0 emery paper. Rough polishing was accomplished with 6 μm diamond on hard paper and 0.3 μm alumina on AB microcloth. Final polishing was achieved with 0.05 μm alumina on AB microcloth. Metallographic examinations were performed on either a B&L Balphot II or a Zeiss Ultraphot metallograph. Most photographic exposures were made under polarized light.

D. Scanning Electron Microscopy

Scanning electron microscope (SEM) examinations were made with an AMR Model 900 scanning electron microscope. In several instances a qualitative surface chemistry analysis was performed on this instrument using a Princeton Gamma Tech Series LS non-dispersive X-ray spectrometer to analyse the characteristic X-rays emitted by the sample. Examinations were made primarily on the longitudinal surface of wire samples with the insulation removed.

In a few instances, the SEM, rather than a metallograph , was used for the examination of transverse sections in order to take advantage of its much greater depth of focus.

E. Electron Microprobe Analysis

Electron microprobe studies were conducted with a Hitachi microprobe and an associated Northern Econ II X-ray spectrometer. This instrument is capable of detecting all elements down to, and including, boron. Both transverse sections, with the insulation intact, and longitudinal surfaces, with the insulation removed, were examined.

III. RESULTS AND DISCUSSION

Figure 1 shows full cross-sectional views of unaged unilay and concentric stranded wire. The results of drawing the wire through a die in order to achieve diameter tolerances are clearly evident in Fig. 1a. The individual strands have been deformed considerably and the radial interstrand contact area, particularly in the outer strands, has been markedly increased. What would normally be a simple longitudinal line contact of adjacent strands is now, in effect, a longitudinal contact surface of significant width. Conditions are thus made ideal for strand blocking at elevated temperatures through the interdiffusion of silver between adjacent strands.

Transverse views of the boundary region between adjacent strands of unaged unilay wire and wire aged for various lengths of time at 150°, 200°, and 230°C are shown in Figs. 2-4.

Figure 2a illustrates a region of unaged wire that had been partially cold-welded during manufacture but which was only weakly bonded and separated during metallographic preparation. The succeeding photomicrographs illustrate how a sound bond is created in these regions when the wire is exposed to elevated temperatures. There is no evidence to indicate that the polyimide insulation contributes in any way to this phenomena. It seems quite clear that the much greater strand blocking and loss of flexibility encountered in unilay wire as compared to concentrically stranded material is due solely to silver diffusion and the much greater interstrand contact area.

The most striking features seen in Figs. 2-4 are the obvious formation of a reaction product at the copper/silver interface and an equally obvious degradation of the silver plating. The extent to which the latter has occurred can be seen more clearly in the SEM photographs of the longitudinal wire surface shown in Figs. 5-7. The beaded or globular appearance of the surface material gives the impression that a process similar to incipient melting has taken place.

Neither metallographic nor SEM observations give any indication that the polyimide/FEP insulation participates in or contributes to the reactions observed. If anything, the insulation appears to be somewhat protective. Cross-sectional views indicate that the reaction product layer is thinner and the surface layer has greater integrity in those regions where the wire strands are in contact with the insulation. The lower

degree of surface degradation in these areas can also be seen in the low magnification SEM photographs shown in Fig. 5b and c. The flat regions on the individual wire strands shown in these photographs are the areas which were in contact with the insulation. The conclusion that the polyimide portion of the insulation does not contribute to the observed reactions is reinforced by an examination of concentrically stranded Teflon-insulated wire aged under the same conditions. As shown in Fig. 8, similar reactions take place.

The massiveness and location (copper/silver interface rather than the silver/air surface) of the reaction product layer was both unexpected and puzzling. The copper-silver binary alloy system undergoes a simple eutectic reaction at 779°C and no intermetallic compounds are formed in the system.[2] McCune et al[1] explicitly noted in their studies of uninsulated wire, aged for 2000 hrs. at 200°C, that no diffusion products were formed at the copper/silver interface and that the only observable reaction was a slight tarnishing or surface oxidation of the silver. In subsequent work, this time on polyimide-insulated wire, McCune[3] noted that metallographic examinations after 2000 hrs. at 200°C gave no indication of a deterioration of the silver plate other than a slight surface oxidation that could be observed at times over 1200 hrs.

An electron microprobe analysis of a unilay sample aged 500 hrs. at 230°C revealed that the reaction product present at

the copper/silver interface is a simple compound of copper and oxygen. Figures 9a and b show the changes in the intensity of the characteristic copper and oxygen X-rays emitted from various points along a scan through an interstrand boundary. The location of the scan trace is nominally represented by the heavy white line superimposed on the reversed-polarity back-scattered electron image of the sample. Numerous cursory scans failed to reveal the presence of any additional elements of significance other than the silver plate between the copper oxide layers and a number of iron-base impurities that occurred well within the copper strands. The oxygen X-ray intensity originating from the silver layer is quite low, indicating that this material is primarily silver metal and not silver oxide (Ag_2O).

The copper oxide layers were unequivocally identified as cuprous oxide (Cu_2O) by means of the energy-intensity relationship of copper L_α X-rays emanating from them. The shape of the L_α emission band is sensitive to the atomic bonding arrangement of the copper atoms as shown schematically for Cu, Cu_2O, and CuO in Fig. 9c. Also shown schematically are the experimentally determined L_α X-ray band profiles originating from the base material and from the oxide. As can readily be seen, the skewed left shape of the latter is uniquely characteristic of Cu_2O for bonding arrangements involving only copper and/or oxygen atoms. The observation of Cu_2O formation at 230°C is of some academic interest in that copper-oxygen phase equilibria studies[2] indicate that below about 375°C, Cu_2O is unstable with respect

to Cu and CuO and copper should oxidize directly to CuO. No effort was made to identify the oxide formed at 200° and 150°C but based on the similarity of its appearance to the oxide formed at 230°C, it is probably Cu_2O also. If so, this would support a contention[4], based on geological considerations, that Cu_2O is stable down to at least 200°C.

The apparently complete disagreement between the metallographic observations that were being made during the course of this investigation and the conclusions reached by McCune et al[1,3], was quite baffling. In order to resolve whatever difference existed, Mr. McCune graciously sent a number of his aged wire samples to AFML for further examination. Figure 10a is a cross-sectional view of an uninsulated SPC unilay wire aged for 2000 hrs. at 200°C. This is the same material investigated by McCune in his first study.[1] As can easily be seen in this photomicrograph, there is no evidence of the formation of cuprous oxide in this material and the integrity of the silver layer has been preserved. The slight deterioration of the silver coating that does occur can best be seen by comparing the SEM photographs of McCune's material in Fig. 11 with the similar views of unaged material shown in Figs. 5a and 6a. Figure 10b is a cross section of polyimide-insulated SPC unilay from McCune's second study.[3] Both the appearance of a cuprous oxide layer and the globularization of the silver coating are similar in every respect to the aged material of this investigation. McCune's conclusion that there was no sign of a deterioration of the silver

plate in this material, only slight oxidation of the silver, was based on 60X and 800X light-microscope examination. At 60X, which is less than half the magnification of the SEM photo in Fig. 5c, the shadowing effect of the silver globules together with the darkness of any regions where the cuprous oxide was exposed could easily be mistaken for a simple silver tarnish. At 800X the depth of focus of a light microscope is so small that hardly anything can be discerned about the curved surfaces of the wire. If the observations at this magnification were confined to the flattened regions originally in contact with the insulation (see Fig. 5c), one could easily be misled as to the true condition of the wire surface.

It can be concluded from a consideration of Figs. 10a and b that as long as the silver coating is intact, oxidation of the copper does not occur. Prior to examining the wire aged at the Hudson Wire Co., the most plausible explanation for the wire deterioration seen in the present study was that oxygen diffused through the silver, oxidizing the copper at the silver/copper interface, and because of an increase in volume of the substrate and suspected poor wetting of the Cu_2O by the silver, the silver coating was broken-up and became globularized due to surface tension effects. Fig. 10 ruled out this explanation completely. Apparently, the deterioration of the silver coating precedes the formation of Cu_2O.

A second explanation, which is consistent with the above observation and also with the earlier conclusion that the insulation is not a contributing factor, stems from the work of

Zakraysek[5] on silver-magnesium-nickel electrical contact alloys. He noted a blistering phenomenon that occasionally occurred when heat treating this alloy in the 300°-700°C range. After establishing the fact that the blistering did not occur when the surface was cleaned, he systematically investigated a series of possible contaminants to determine the origin of the effect. The results of his work clearly established that trace amounts of adsorbed sulfur were responsible for the phenomenon. Zakraysek further showed that sulfur had the same effect on silver of 99.99% purity.

The blistering phenomenon observed by Zakraysek is strikingly similar to the beaded appearance of the silver plating on the aged wires of this investigation. Many of the photomicrographs that he presents show surfaces that closely resemble those shown in Figs. 5-7. Zakraysek also conducted a sphere growth rate study as a function of temperature over the range 300° to 600°C. At 500°C, the only temperature at which he made a complete series of measurements as a function of time, the spheres tended to attain a constant size of 5.0 to 6.5 μm after a period of 45 min. Figure 12 illustrates the growth rate of the silver globules observed in this investigation. Although the temperature is much lower and a considerably longer time is involved, the globules appear to be reaching a constant size within the same range observed by Zakraysek.

The similarity of appearance and terminal sphere size are regarded here as indirect evidence that the phenomena observed by

Zakraysek and in this investigation are the same. Zakraysek concluded from his investigation that--"silver blistering is due to incipient melting caused by trace amounts of sulfur". This is a highly improbable explanation in view of the known phase equilibria of the silver-rich silver-sulfur system[2], which indicates that the lowest temperature for liquid formation is 804°C. As Zakraysek notes in his paper, Perdereau and Rhead[6] have observed that adsorbed sulfur causes a large increase in the surface self-diffusion of silver. A much more plausible explanation is that the phenomenon is simply a spheriodization process resulting from increased silver surface diffusion rates and surface tension forces.

A considerable amount of effort was expended in attempting to establish the existence of sulfur contamination through characteristic X-ray analysis both with the scanning electron microscope and with the electron microprobe. Observations on the longitudinal surfaces of stripped, aged and unaged, wire identified isolated patches or regions containing sulfur but a continuous film of significant thickness could not be detected. If, as expected, the spheroidization process is entirely a surface phenomenon, a film only a few atom monolayers in thickness would be needed. An electron microprobe, operated conventionally, does not have sufficient sensitivity to detect elemental concentrations corresponding to this level of contamination. Unambiguous proof of the existence of a very thin adsorbed layer would require the use of a surface analytical technique such as Auger spectroscopy

or ion scattering spectroscopy. However, indirect evidence for its existence was found in microprobe studies of wire cross sections.

In viewing cross sections of the stranded wire, the electron beam of the microprobe is parallel to the longitudinal surface of the individual strands. When the beam is positioned over a free edge, i.e., one that has not been rounded or smeared in the polishing operation, the path length of the electrons within the surface layer and the total surface area irradiated by the beam will be many times larger than in the normal case where the beam is directed perpendicular to the surface. If the surface is favorably oriented toward the X-ray detector, the characteristic X-rays emitted by surface atoms and subsequently detected will be proportionally larger.

Most of the exposed wire strand edges, seen in Fig. 1a for example, are too rounded or smeared for the above effect to occur. However, at many of the V-shaped regions, where two individual strands come into contact, the edge is relatively sharp. Regions of this type are shown in Figs. 2-4, particularly in Fig. 4c. In many instances when the electron beam was positioned over one of these edges, sulfur could be detected. When the beam was withdrawn from the edge, but still positioned over the silver layer, no sulfur could be detected. Thus the sulfur observed was surely associated with the vertical (outside) surface. The frequency with which sulfur detection occurred was much greater than could be explained by a chance cross-sectioning through the isolated sulfur-bearing areas noted earlier.

While the above observations are indirect and cannot, therefore, be regarded as rigorous, they do strongly support the existence of a sulfur-containing contamination layer on the surface of the silver-plated wire. Actually, it is not too surprising that this should be the case. The high sulfur content of an industrial atmosphere is well known. Furthermore, the wires are plated by one manufacturer, then shipped to a second manufacturer for application of the insulation. Although the plated spools of wire are presumably protected by some type of container during shipping and while stored at the two manufacturing facilities, the degree of protection offered may not be sufficient and/or the length of time during which protection is not present may be too long to prevent the level of contamination proposed here. The possibility also exists that, over long periods of time after the insulation has been applied, contamination could occur by interstrand gaseous diffusion from the wire ends. This may indeed increase the degree of contamination but is not considered the primary process.

It should be noted that the extensive testing of uninsulated wires conducted by McCune et al[1] was performed on material that had been plated only a short time prior to conducting the tests. They took this course of action in order to minimize the effects of shelf-life. Since the wire would presumably have adsorbed much less sulfur than wire undergoing normal handling, this seemed to offer a plausible explanation for the differences in deterioration observed between the uninsulated and insulated wires

of McCune's investigation and this study. In order to assess the effect the difference in access to oxygen might have on the results, a series of insulated wires were stripped of their insulation and aged at 200° and 230°C.

The appearance of the aged, stripped wires was quite suprising. The outer strands, at least, did not show any evidence of the silver spheroidization observed on insulated wires but appeared to be covered with an oxide. The morphology of the oxide was quite varied. Figure 13a illustrates an area typical of a large fraction of the surface. Furrowed regions, nodules, and a few whiskers can be seen. Figure 13b shows a higher magnification view of a furrowed region. Superimposed on this photograph is a copper K_α X-ray emission scan which was made horizontally across the surface through the white dot seen in the lower center of the picture. Following the course of this scan through the dot shows that the overlying material is copper-rich. Figure 14 depicts a region containing mostly nodules. The X-ray scans through the white dots in the center of these photographs shows that the nodules are copper-rich while the background material is silver-rich. Oxygen X-ray scans of the furrowed regions (Fig. 13) and the nodules (Fig. 14) reveal that both are copper oxide. Figure 15 shows two types of whisker colonies. In Fig. 15b, the whiskers can be seen growing out of the nodules.

The stark contrast between the significant oxidation of stripped wires aged 500 hrs. at 200°C in this investigation

and the almost imperceptible tarnish seen on McCune's uninsulated wire aged 2000 hrs. at the same temperature can only be explained by the fact that the latter was aged on spools. With this practice, wire is removed for testing at the end of each time increment. Consequently, the material aged for long periods of time is protected by many outer layers of wire. The present observations indicate that the oxygen availability must be severely restricted under these conditions and the test cannot therefore be considered representative of true free airflow. This contention was supported by an examination of some additional wire obtained from the Hudson Wire Co. study which had evidently seen a greater airflow exposure. This material was a solid AWG 28 SPC wire also aged 2000 hrs. at 200°C. Much of the wire was covered with oxide similar to that in Fig. 13 but large regions also contained nodules and whiskers as can be seen in Figs. 16 and 17. The density of both oxide and whiskers on these wires was much greater than on the AFML-aged material, presumably due to the longer exposure time. The crater-like features seen in Fig. 17 were not observed on material aged in the present study, but may be an advanced stage of deterioration occurring in the vicinity of one of the isolated regions containing higher than normal sulfur mentioned earlier. These regions (see Fig. 18) frequently contain carbon and chlorine in addition to sulfur in their interior, and traces of sulfur and chlorine, but no carbon, on the immediately adjacent material. Such contaminated regions are found on both inner and outer strands; however, on the outer

strands the chlorine level is noticeably higher than the sulfur level.

Examination of the inner strands of the aged, stripped wires revealed spheroidization of the silver similar to that seen in the aged, insulated wires. The surface of an inner strand is shown in Fig. 19. CuK_α and AgK_α X-ray scans through the white dots located in the center of the photographs show that the globules are silver-rich and not the same as the copper-rich nodules noted on the outer strands (Fig. 14). Apparently, when the availability of oxygen is restricted, the spheroidization process can occur. In the presence of free flowing air, however, the rapid formation of a copper oxide layer overlying the silver prevents spheroidization.

The mechanism by which a copper oxide layer is deposited or grown on the outside surface of the silver plating is not clear. Cross sections of oxidized strands (see Fig. 20) reveal that breaks in the silver plate are often present and that the region underlying the silver is sometimes oxidized (Fig. 20a), but more frequently is cavitated (Figs. 20b,c). Readers acquainted with the so-called 'red plague' corrosion of silver-plated copper wires[8] will note a similarity in the appearance of that phenomenon and the cross-sectional views of Fig. 20. 'Red plague' is normally attributed to the galvanic attack of copper at existing breaks in silver plating in the presence of moisture and oxygen. The plating defects are presumed to occur during the manufacturing process.

Despite the similarity in appearance, the possibility that the attack during aging involves galvanic corrosion appears remote. First, an aqueous electrolyte could not be expected to persist at 200°C. Second, an unreasonable number of plating defects would need to be present to account for the degree of attack observed. It seems much more likely that localized breakdown of the silver layer occurs during the aging, probably at the sites of the aforementioned contaminated regions. This is followed by oxidation of the copper by both oxygen and any water vapor that may be present. Copper atoms apparently migrate through the silver orifice by surface diffusion with the result that oxidation occurs both on the outside surface and within the cavity underlying the silver. As the break in the silver tends to become plugged with oxide, it is quite likely that the rate of oxidation within the cavity diminishes and that the primary oxidation takes place on the outside.

Whether or not the deterioration of both insulated and stripped SPC wire observed at 200°C and above represents a serious or even moderate limitation to its use at that temperature is difficult to evaluate. In the case of insulated wire, there is no doubt that the spheroidization of the silver plating, followed by loss of plating continuity and concurrent oxidation of the copper conductor, results in a decrease in conductor cross section that will ultimately lead to an increase in electrical resistance. The rate at which the oxidation occurs can be

seen in Fig. 21, which shows the oxide film thickness as a function of time and temperature. It is obvious that the importance of the loss in conductivity resulting from oxidation will increase with decreasing wire size. If, for No. 26 wire (which for added strength employs a copper alloy containing small amounts of cadmium and chromium rather than pure copper), the continuity of the silver is completely lost and the rate of oxidation is comparable to that for pure copper (Fig. 21), an 8% loss in conductivity would occur in 500 hrs. at 200°C. For No. 24 wire, the loss would reach approximately 6.5%. These estimates actually represent upper bounds since they do not take into account the fact that substantial continuity of the silver appears to be retained in the interstrand contact regions. As can be seen from Fig. 21, the rate of oxidation decreases with time, indicating that the oxide layer is protective. While both the oxidation and the conductivity loss will increase with time, therefore, it will do so at a continuously decreasing rate.

In wire stripped of its insulation, as would be typical of wire terminations, the deterioration observed in this study may have a different effect on service performance. Regardless of the mechanism by which the integrity of the silver plating is violated and the growth of bulk copper oxide and whiskers together with the cavitation of the copper underlying the silver occurs, an ideal site for corrosion at ambient temperatures is created. All

that is lacking is the presence of moisture to act as an electrolyte. If moisture collects at one of these sites, either by condensation from the atmosphere or direct contact with water, two types of galvanic attack could occur. The first is of the dissimilar metal type ('red plague') in which the silver acts as a cathode and the copper acts as the anode. The second involves the creation of an oxygen concentration cell. As the oxygen within the cavity is used up in oxidizing copper it will not be readily replenished due to the restriction of the small orifice which will be at lease partially plugged with oxide. This will establish a potential difference between the cavity and the outside surface leading to anodic dissolution of the copper within the cavity. The copper ions will then migrate out of the cavity where they will be oxidized. Since the corrosive attack would continue incessantly at ambient temperature, local dissolution and failure of the entire conductor cross section would ultimately occur. The length of time required to create a susceptible site is unknown. Since their creation could constitute a serious problem, they should be avoided by adequately sealing wire terminations to prevent the access of oxygen and moisture.

The degree to which the electrical and mechanical performance and reliability of insulated SPC wire is degraded by silver spheroidization, conductor oxidation, and strand blocking can only properly be judged by functional testing. The study conducted by McCune et al[1] on uninsulated wire is not applicable

for the reasons noted earlier. In his more recent study on insulated wire, McCune[3] found that the flex life of No. 20-Kapton-insulated concentric wire, thermally aged at 200°C, first increased with time, presumably due to annealing, then decreased to a level approximately 50% greater than for unaged wire. Unilay wire exhibited a similar initial increase in flex life followed by a continuous decrease that reached a level of about 55% of that for unaged wire after 2000 hrs. of exposure. Electrical properties were not measured.

Smith[9] tested both the electrical and flex life properties of No. 22 unilay and concentric wire at 230°C for periods up to 500 hrs. and concluded that there were no functional differences between the two types of construction. His data indicate that the flex life of both types of wire decrease with time, but only nominal changes in electrical resistivity are observed. In the case of unilay wire the resistance first decreased (again probably due to annealing) and then increased to a level, after 500 hrs., that was still approximately 2% lower than that of unaged wire. The latter result is difficult to reconcile with the degradation observed in the present study. By making a substantial allowance for the retention of silver continuity at interstrand contacts, an increase in resistance of more than 4% would have been predicted. The only rational explanation for the apparent discrepancy is that there must be considerable variation in the degree to which wire becomes contaminated during manufacture and, hence, in the extent of deterioration during thermal aging.

The phenomenological observations of this study together with the limited functional testing conducted by McCune[3] and Smith[9] indicate that for current and near-term aircraft, the thermal aging of FEP/polyimide-insulated SPC wire does not constitute a problem. For all presently envisioned applications, exposure to temperatures near the present rating (200°C) are of very short duration. On the other hand, the results of this investigation indicate that a 200°C rating should not be assumed valid for indefinite usage. In this respect the governing Military Specifications are misleading. A multiple rating involving a more moderate temperature for extended usage, e.g., 150°C, coupled with a time-temperature factor for use at more elevated temperatures would be more appropriate. The importance of establishing a time-temperature factor can only be determined from the results of more extensive functional testing than has been performed to date. Such testing should be performed on material from more than one manufacturer and of more than one shelf-life in order to include the effects of differing degrees of contamination.

IV. SUMMARY AND CONCLUSIONS

1. Insulated and stripped, unilay and concentric SPC wires were aged for various times at 150°, 200°, and 230°C to determine whether or not FEP/polyimide insulation contributes in any way

to the noticeable strand blocking that occurs on exposure to elevated temperatures. It was concluded that the insulation is not a factor and that the phenomenon is due entirely to the interstrand diffusion of silver. The more severe strand blocking experienced by unilay wire, compared to concentric construction, is due solely to an inherently greater interstrand contact area which is further enhanced by plastic deformation when the stranded wire is drawn through a die. During the course of the study, two types of conductor degradation, unrelated to strand blocking, were identified.

2. In wire protected by insulation, the silver coating undergoes a spheroidization process which, in appearance, looks as though incipient melting had occurred. The spheroidization first leads to a thinning of the silver layer and ultimately, to a complete loss of coating integrity. The loss of coating continuity and the oxidation of the copper, which is occurring simultaneously, should both lead to a decrease in electrical conductivity. For No. 26 wire this could result in a decrease of up to 8% in 500 hrs. Despite the appearance of the phenomenon, incipient melting is ruled out as a cause. Instead, it is attributed to surface tension forces and vastly increased silver surface diffusion rates stemming from trace sulfur contamination of the surface. The contamination is believed to occur via airborne sulfur containing gases between the plating and insulating processes.

3. In wire stripped of its insulation, as would be typical of termination points, the deterioration is characterized by the growth of bulk copper oxide and whiskers on the outside surface of the silver coating and a cavitation of the underlying copper. This type of phenomenon has the appearance of a mild form of 'red plague' galvanic corrosion. 'Red plague' is ruled out as a cause, however, due to the absence of a suitable electrolyte at elevated temperature. It is thought, instead, that the incursion through the protective silver layer may be related to the presence of contaminated regions containing sulfur, chlorine, and carbon that were identified by electron microprobe analysis. This is followed initially by oxidation of the underlying copper and eventually by the diffusion of additional copper to the surface where it is oxidized to form a surface oxide layer. Regardless of its cause, the resulting cavity and its overlying silver layer constitute an ideal site for galvanic corrosion at ambient temperature if the region is exposed to moisture and oxygen. Since the attack would be highly localized and ultimately end in the rupture of the conductor, it is recommended that wire terminations exposed to thermal aging be sealed.

4. The degradation found in silver-plated copper aircraft wire during thermal aging indicates the need for caution in applying Mil Spec ratings to applications where high reliability and long service life at elevated temperatures are desired. There does not appear to be any reason for concern in current or near-term applications since the exposure to temperatures near the present

200°C rating are expected to be of short duration. However, this rating should not be assumed valid for indefinite usage. The practice of establishing a fixed temperature rating is unrealistic in that it overstates the true temperature capability for long term applications and understates it for short-term applications. A dual rating consisting of a moderate temperature for indiscriminate use (150°C, for example) and a limiting time-temperature factor for higher temperature applications would be more appropriate.

V. REFERENCES

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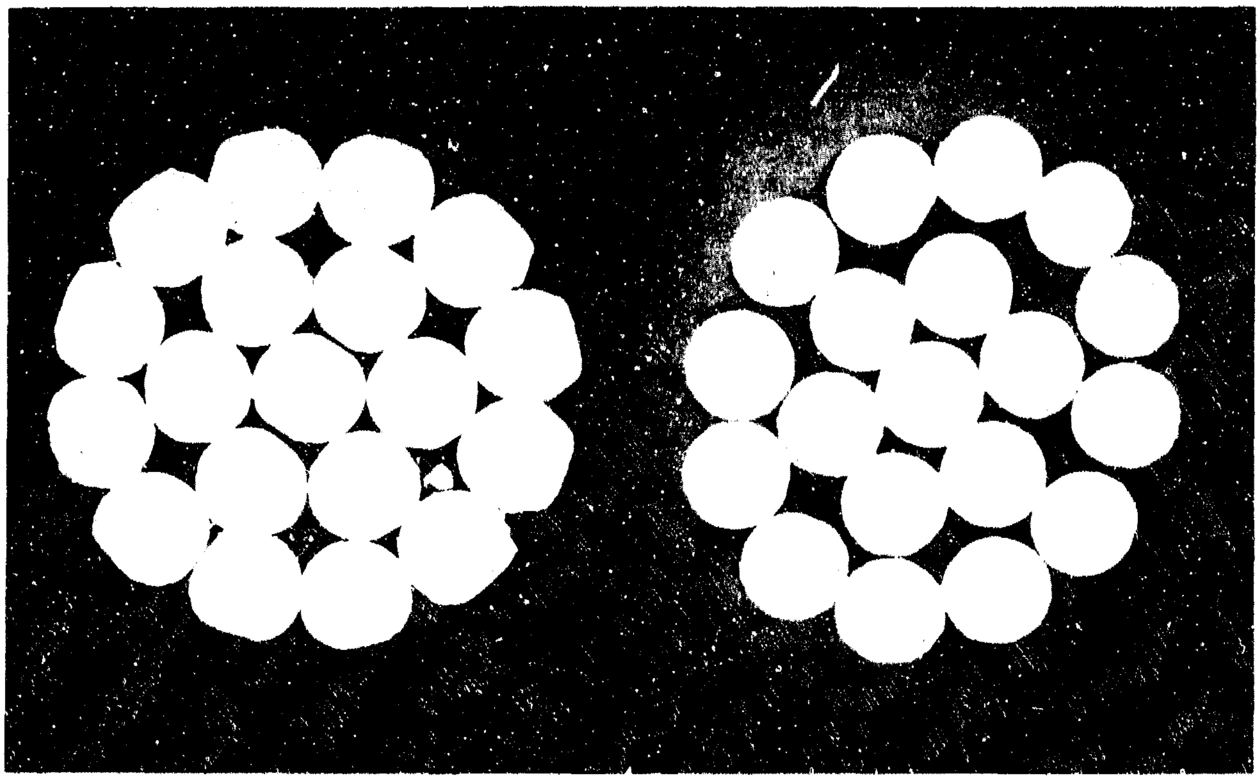
7. T.B. McCune, private communication.

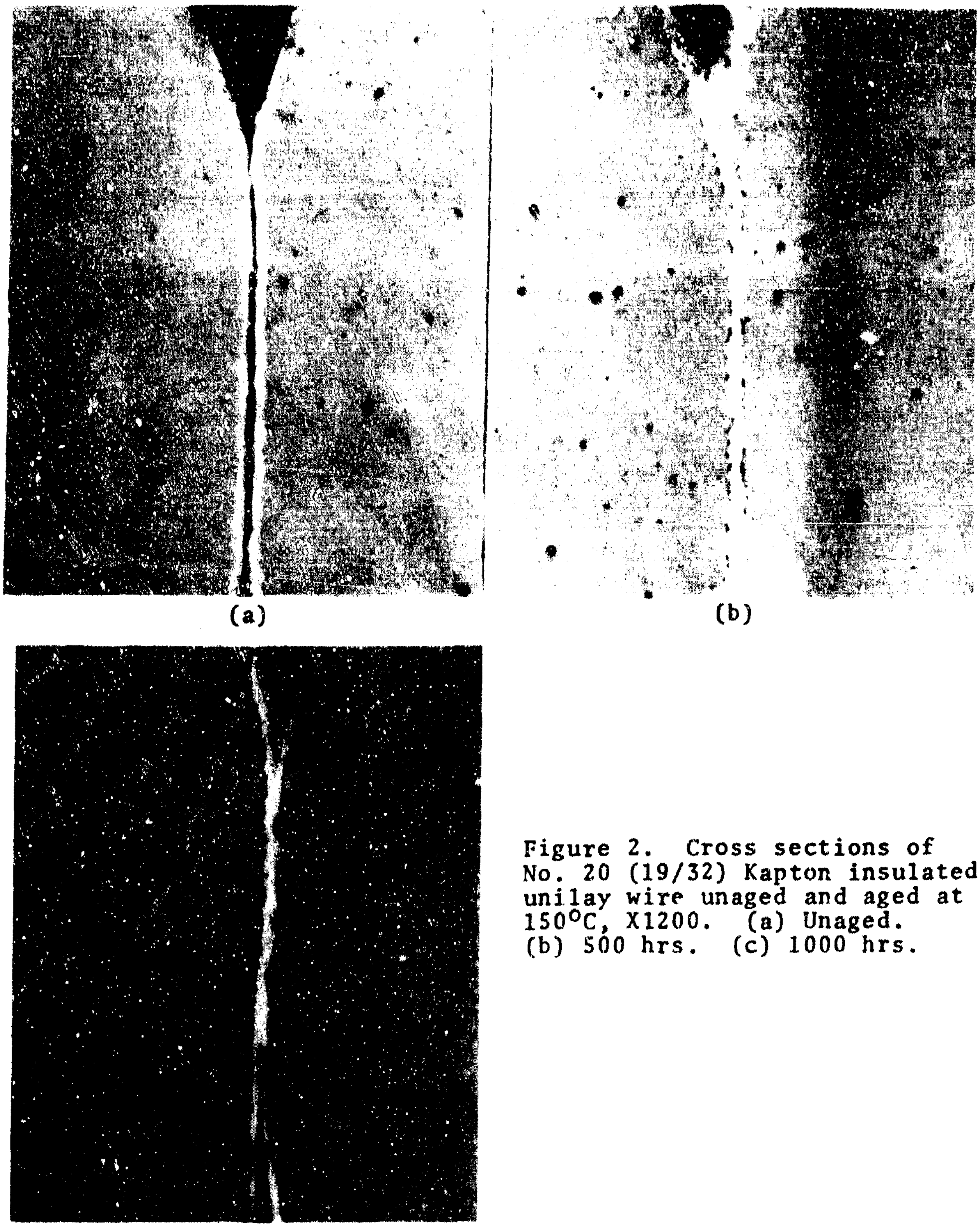
8. W.T. McFarlen, "Corrosion of Silver-Plated Copper Wire ("Red Plague")", presented at the Sixth Annual Bureau of Naval Weapons Symposium on Advanced Techniques for Aircraft Electric Systems, Wash., D.C., Oct. 1965.

9. R. Smith, "Functional Testing of Unidirectional and Concentric Stranded Conductor", Rpt. to the SAE A-2H Committee on Aerospace Wire and Cable, Oct. 1971.



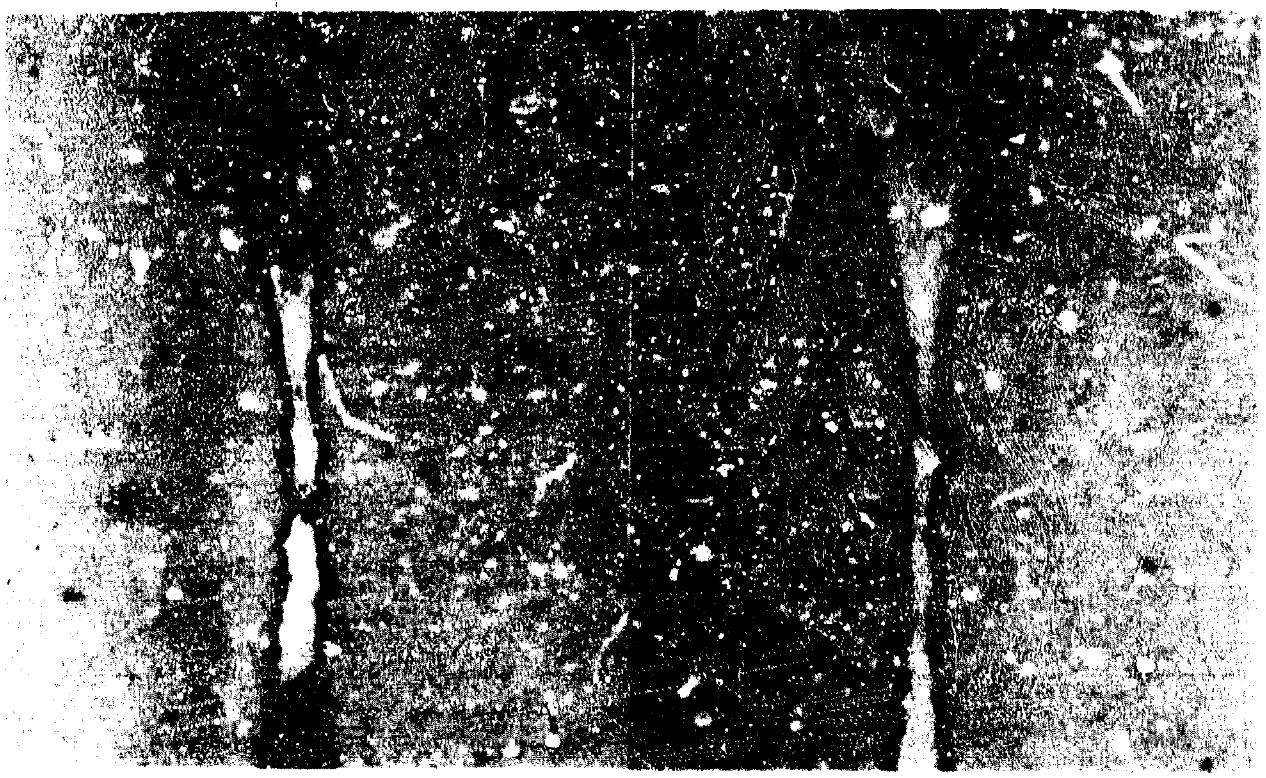
(a) (b)

Figure 1. Cross-sectional views of unaged wire. (a) No. 20 (19/32) Kapton insulated unilay wire, X65. (b) No. 18 (19/30) Teflon insulated concentrically stranded wire, X50.



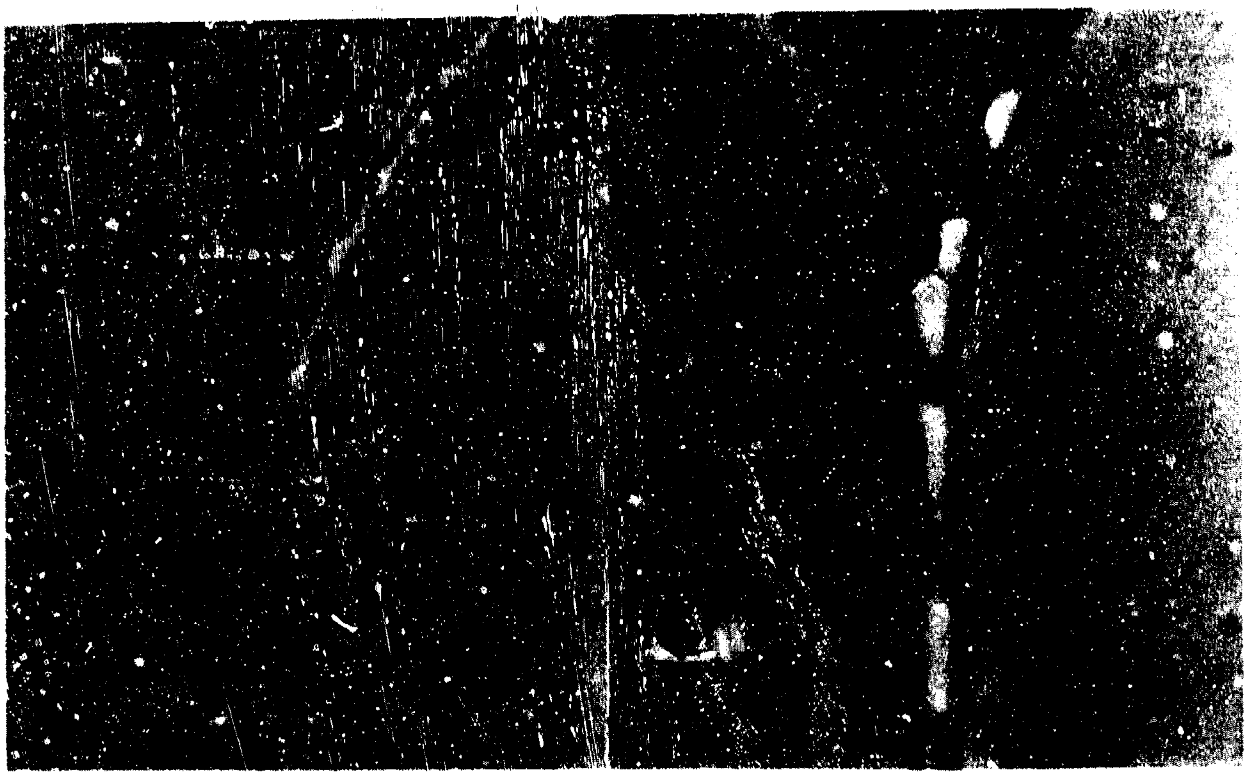
(a) (b) (c)

Figure 2. Cross sections of No. 20 (19/32) Kapton insulated unilay wire unaged and aged at 150°C, X1200. (a) Unaged. (b) 500 hrs. (c) 1000 hrs.



(a) (b)

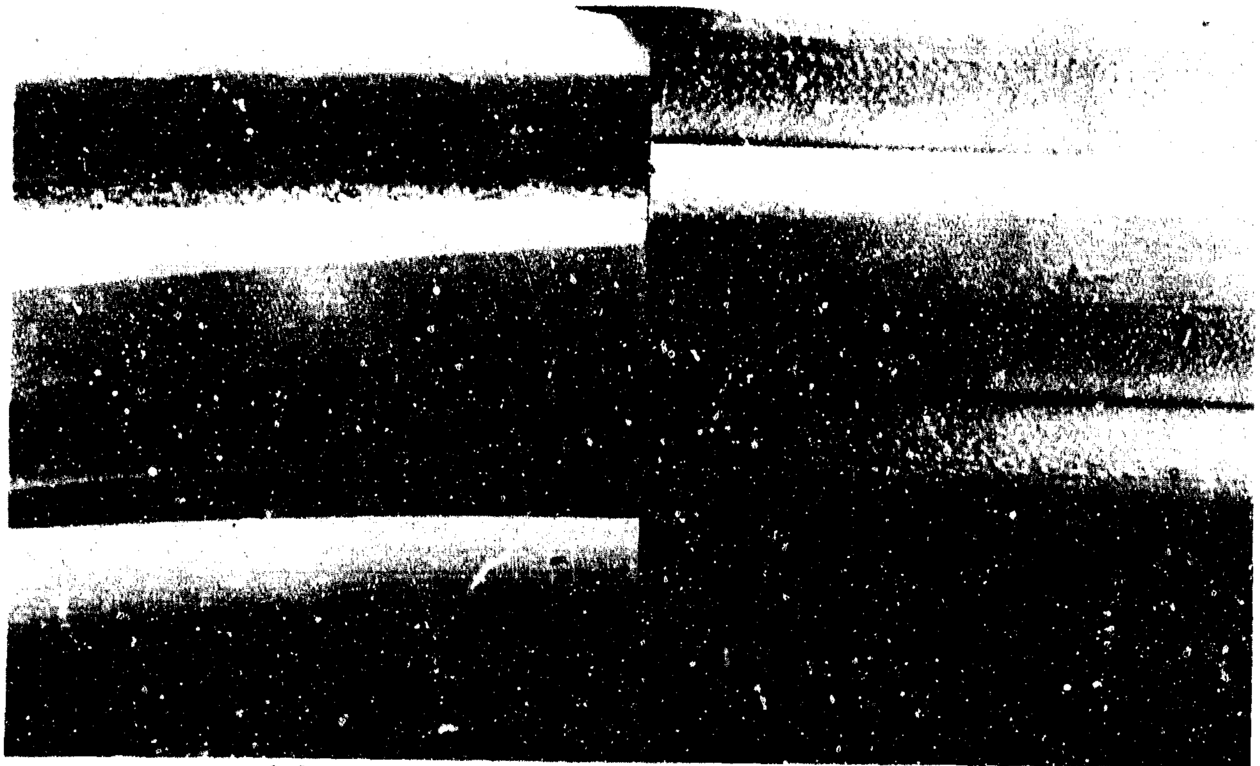
Figure 3. Cross-sections of No. 20 (19/32) Kapton insulated unilay wire aged at 200°C, X1200. (a) 500 hrs. (b) 1000 hrs.



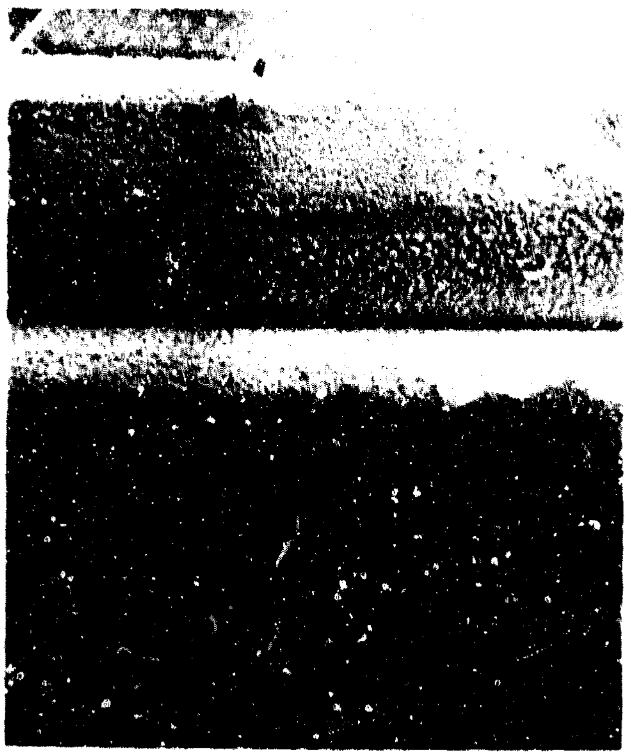
(a) (b)

(c)

Figure 4. Cross-sections of No. 20 (19/32) Kapton insulated unilay wire aged at 230°C, X1200. (a) 125 hrs. (b) 264 hrs. (c) 500 hrs.



(a) (b)



(c)

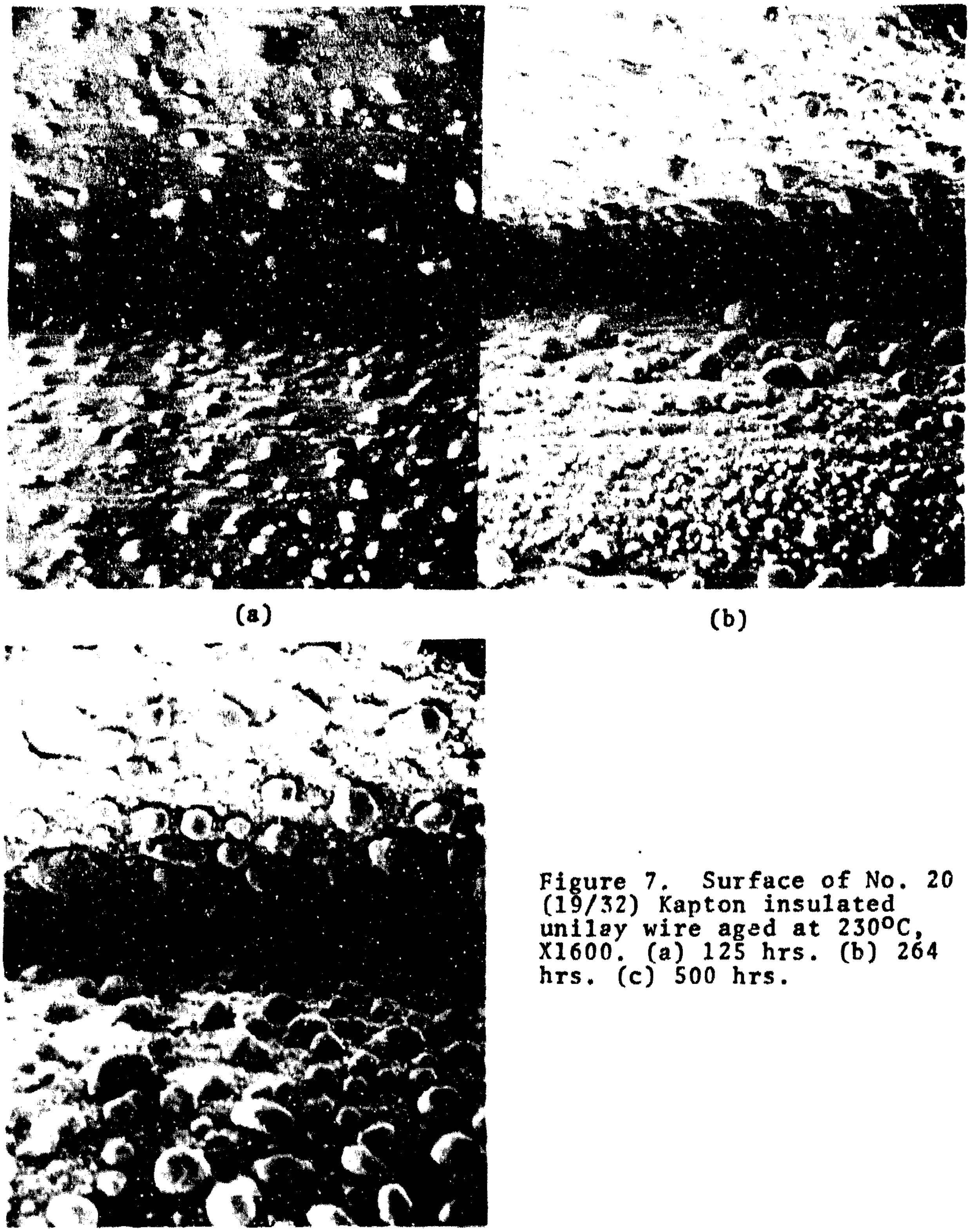
Figure 5. Surface of No. 20 (19/32) Kapton insulated unilay wire, unaged and aged at 200°C, X170. (a) Unaged. (b) 500 hrs. (c) 1000 hrs.

(a)

(b)

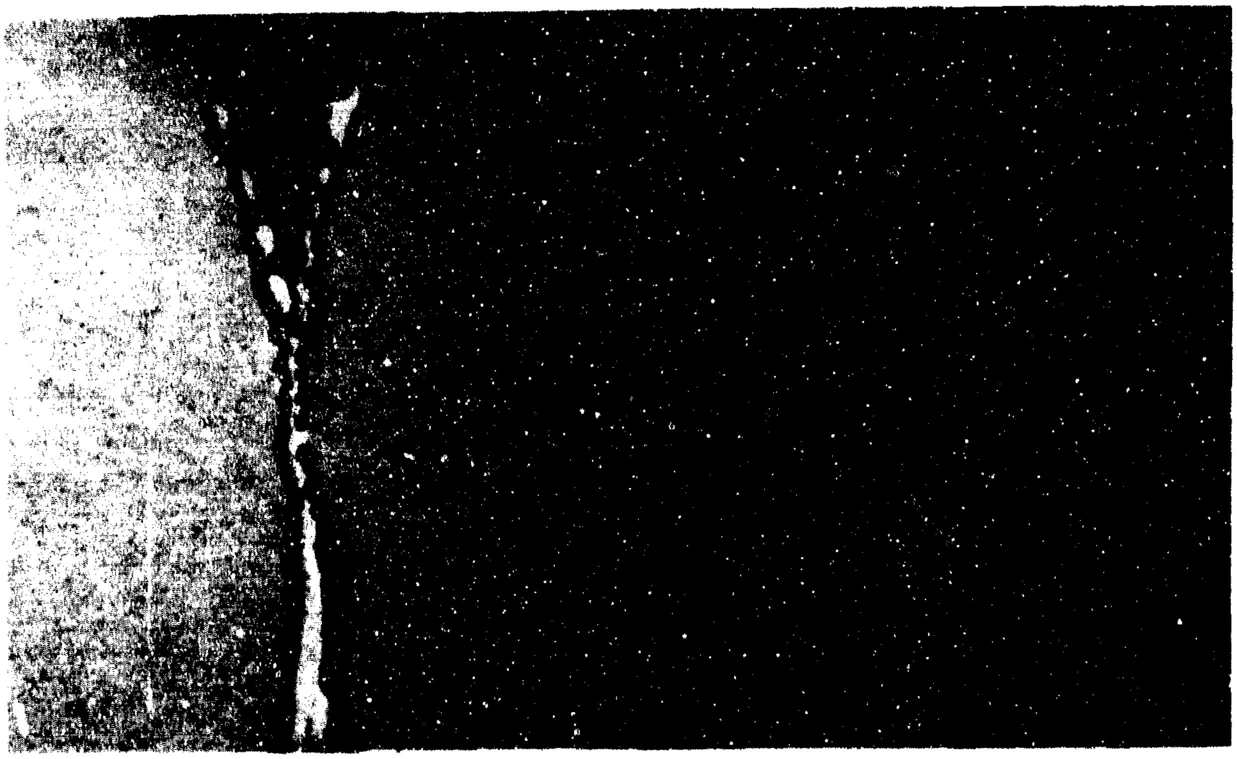
(c)

Figure 6. Surface of No. 20 (19/32) Kapton insulated unilay wire, unaged and aged at 200°C, X1600. (a) Unaged. (b) 500 hrs. (c) 1000 hrs.



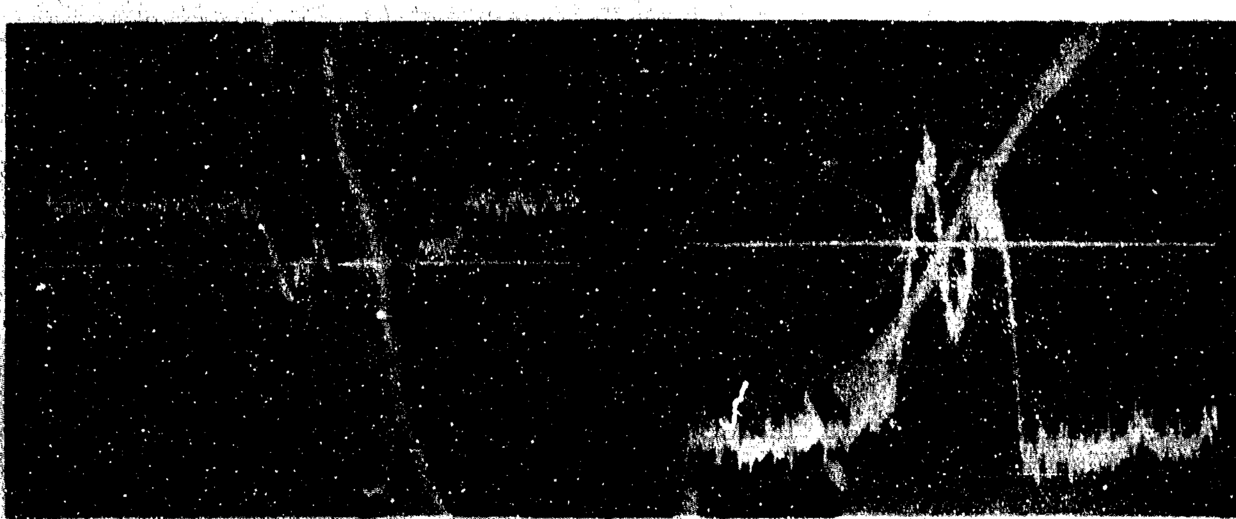
(a) (b) (c)

Figure 7. Surface of No. 20 (19/32) Kapton insulated unilay wire aged at 230°C, X1600. (a) 125 hrs. (b) 264 hrs. (c) 500 hrs.

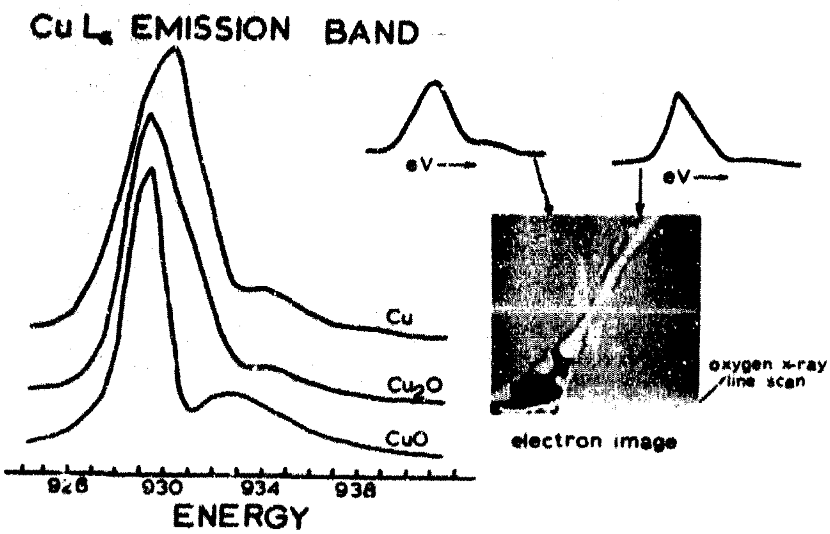


(a) (b)

Figure 8. Cross-sections of aged No. 18 (19/32) Teflon insulated concentric wire. (a) 1000 hrs at 200°C, X1200. (b) 500 hrs at 230°C, X400.

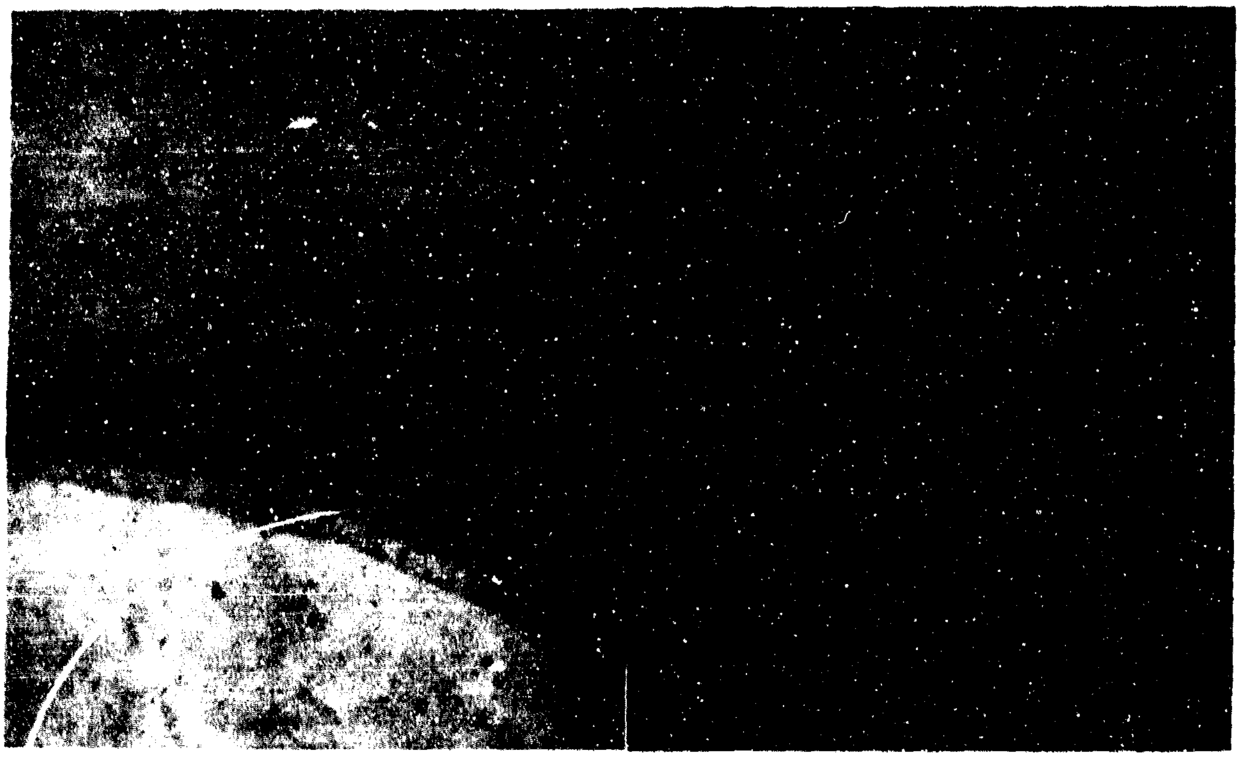


(a) (b)



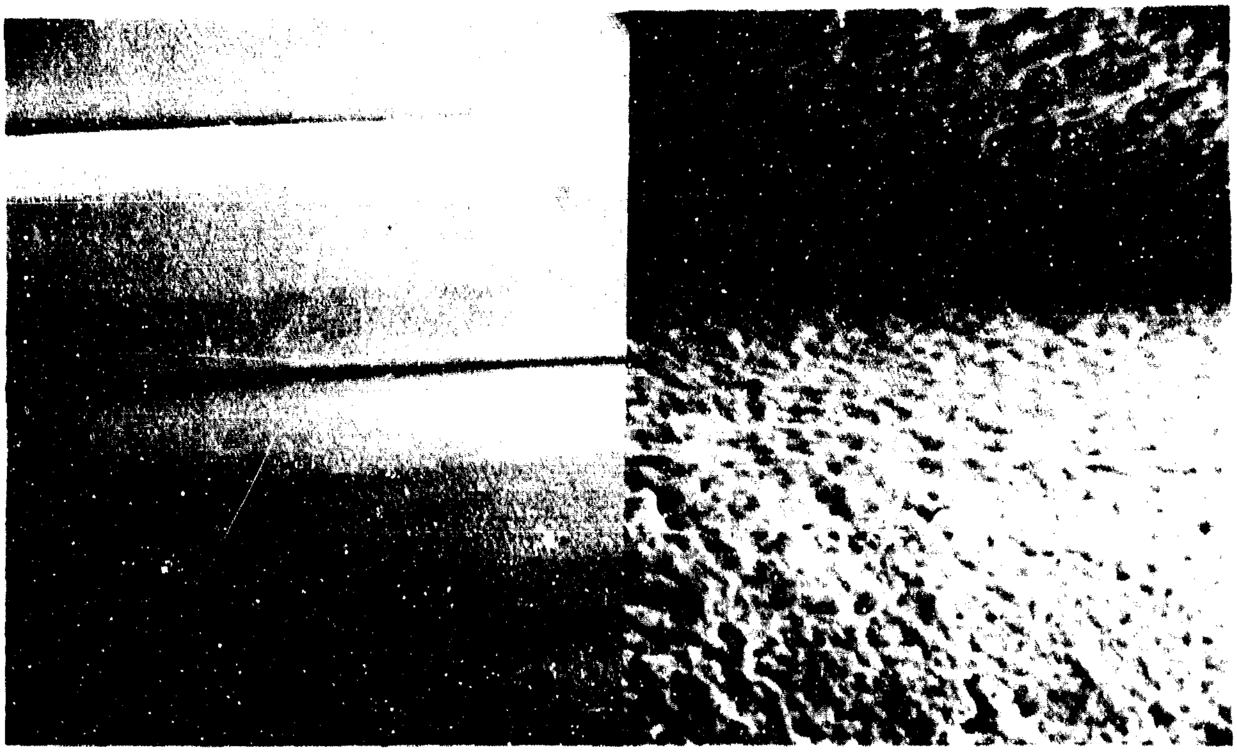
(c)

Figure 9. Electron microprobe scans of No. 20 (19/32) Kapton insulated unilay wire aged 500 hrs at 230°C. (a) Reverse electron image with Cu K_α X-ray emission scan, X2880. (b) RE image with O_2 K_α X-ray emission scan, X1440. (c) Cu L_α X-ray emission band profile for Cu, Cu_2O, CuO.



(a) (b)

Figure 10. Unilay wire aged by the Hudson Wire Co. 2000 hrs at 200°C, X1200. (a) Uninsulated No. 18 (19/30). (b) Kapton insulated No. 20 (19/32).



(a) (b)

Figure 11. Surface of No. 18 (19/30) uninsulated unilay wire aged 2000 hrs at 200°C by the Hudson Wire Co. (a) X160. (b) X1600.

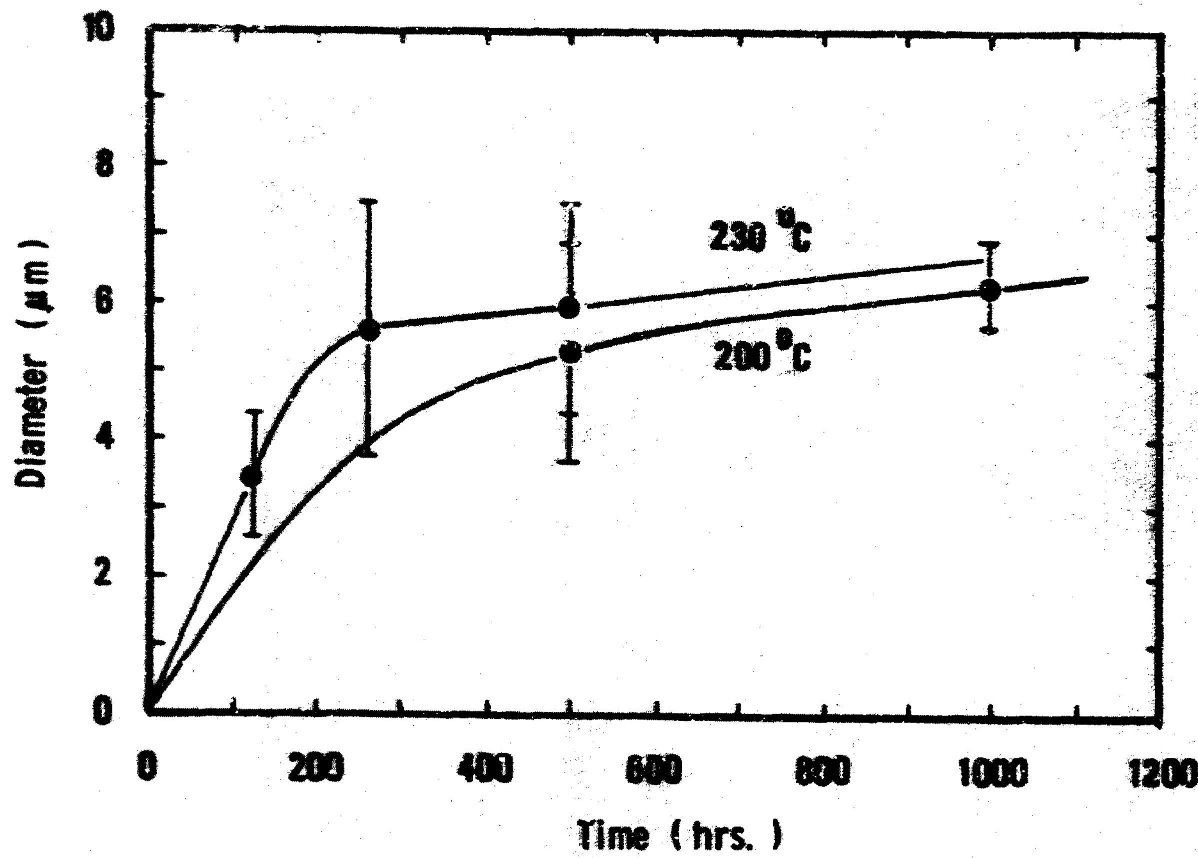


Figure 12. Diameter of larger silver globules on No. 20 (19/32) Kapton insulated unilay wire as a function of time and temperature.

(a)

(b)

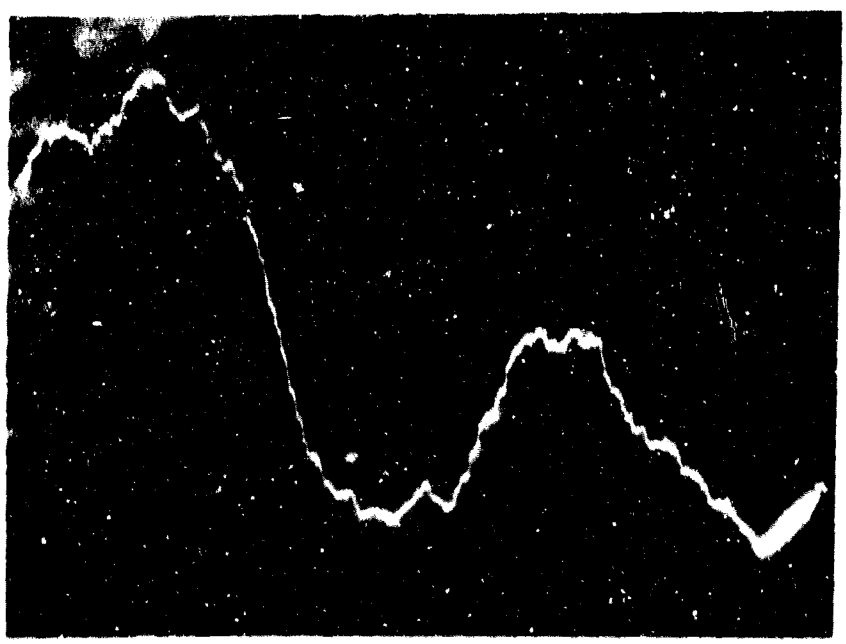
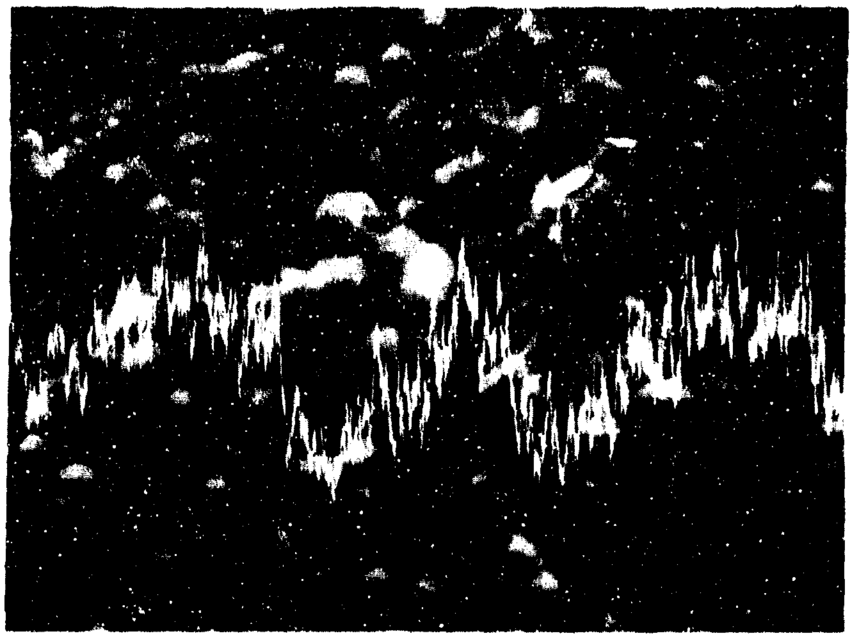


Figure 13. Surface of No. 20 (19/32) Kapton insulated unilay wire aged 500 hrs at 200°C with insulation removed prior to aging. (a) Typical surface of outer strands, X1600. (b) X5000 with superimposed CuK_{α} X-ray emission trace.

(a)



(b)

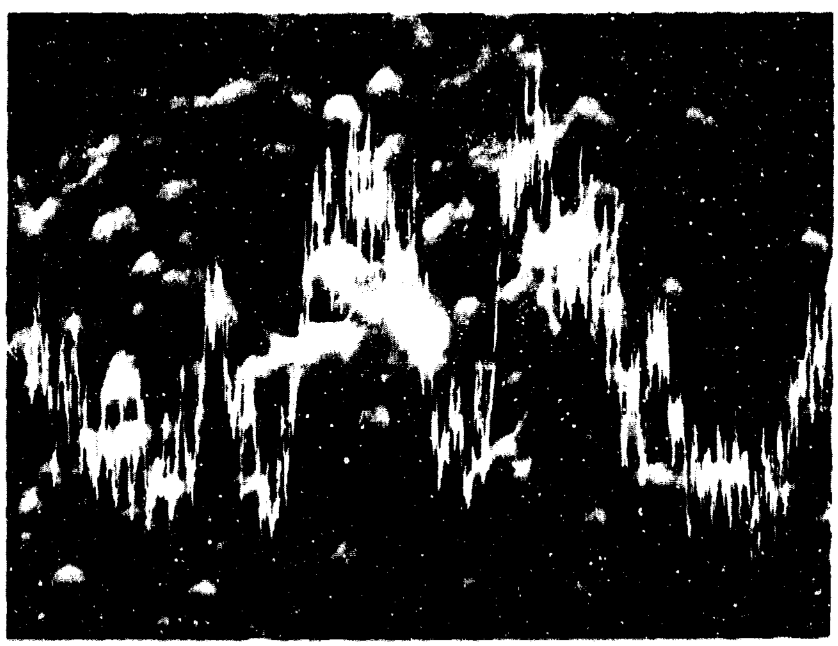


Figure 14. Surface of No. 20 (19/32) Kapton insulated unilay wire aged 500 hrs at 200°C with insulation removed prior to aging. X-ray emission scans superimposed on structure of outer strands in regions containing copper oxide spheres, X5000. (a) AgK_{α}. (b) CuK_{α}.

Fig. 15 (a)   Fig. 15 (b)

Fig. 16

Figure 15. Surface of No. 20 (19/32) Kapton insulated wire aged 500 hrs at 200°C with insulation removed prior to aging. Regions containing whiskers are shown. (a) X1000. (b) X2500.

Figure 16. Surface of AWG 28 uninsulated solid wire aged 2000 hrs at 200°C by the Hudson Wire Co., X2500.

(a)

(b)

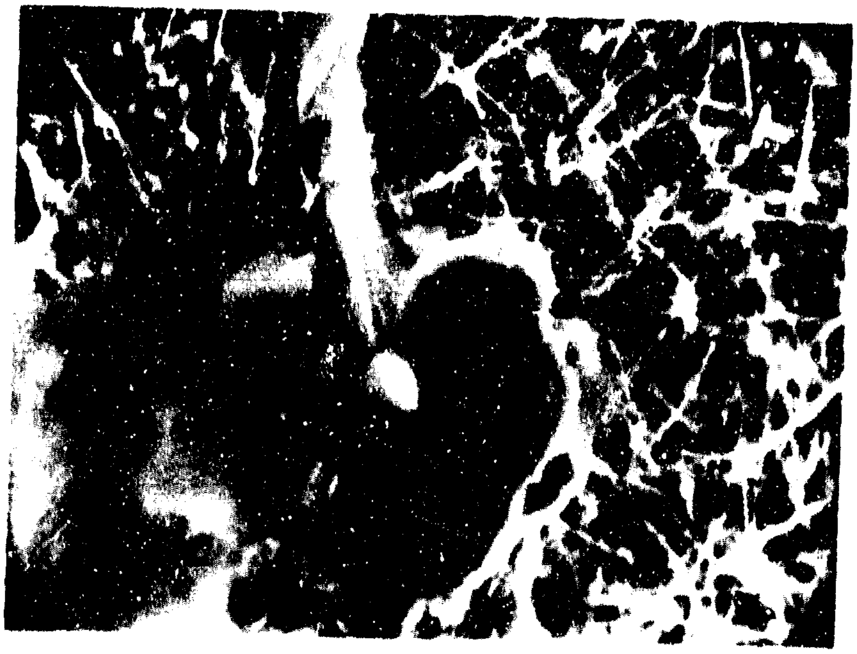


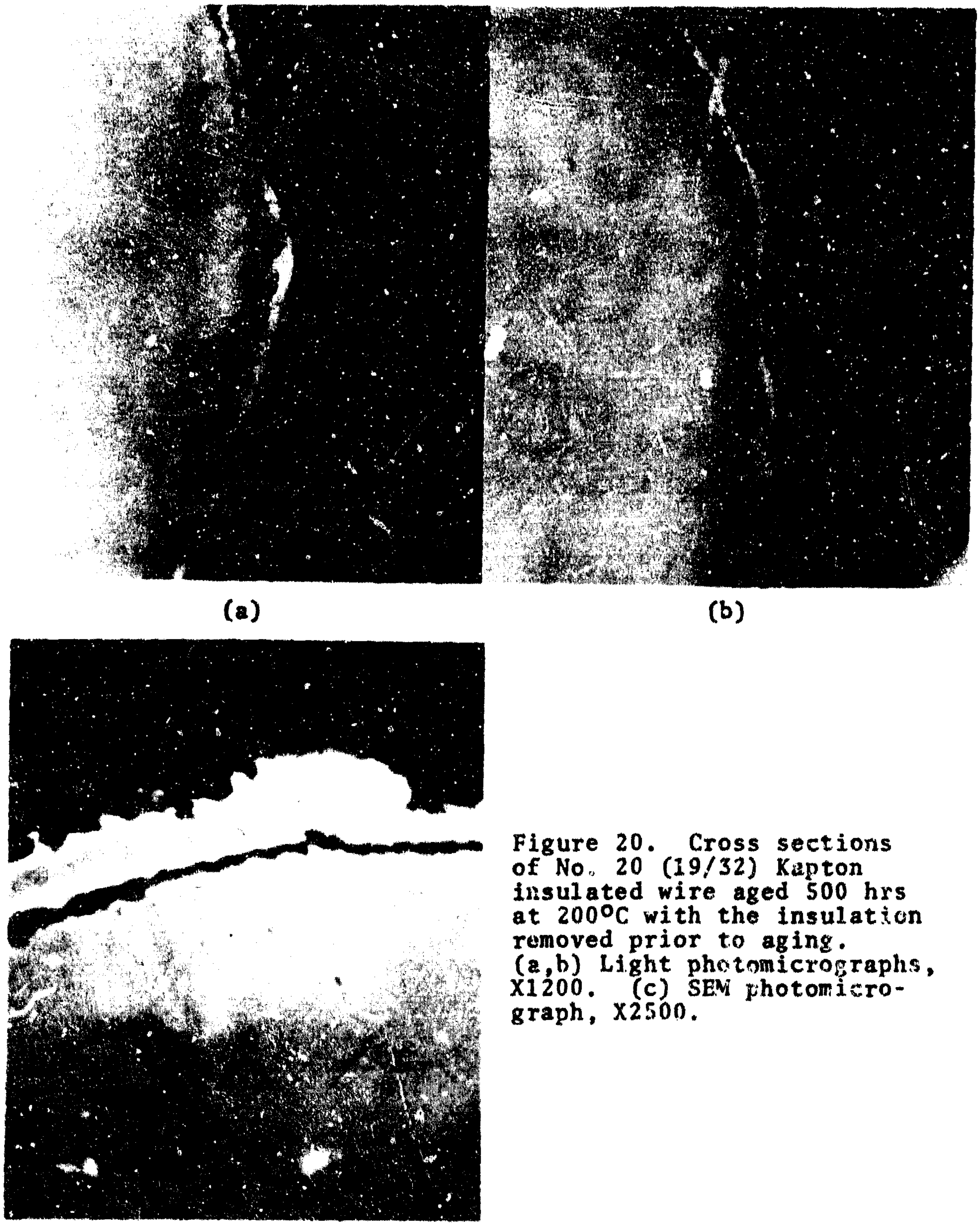
Figure 17. Surface of AWG 28 uninsulated solid wire aged 2000 hrs at 200°C by the Hudson Wire Co. (a) X500. (b) Same area, X2500.

Figure 18. Surface of No. 20 (19/32) Kapton insulated wire aged 500 hrs at 200°C with the insulation removed prior to aging. Typical contaminated area, X1000.

(a)

(b)

Figure 19. Surface of No. 20 (19/32) Kapton insulated wire aged 500 hrs at 200°C with the insulation removed prior to aging. X-ray emission scans superimposed on structure of inner strands, X5000. (a) CuK_{α}. (b) AgK_{α}.



(a) (b) (c)

Figure 20. Cross sections of No. 20 (19/32) Kapton insulated wire aged 500 hrs at 200°C with the insulation removed prior to aging. (a,b) Light photomicrographs, X1200. (c) SEM photomicrograph, X2500.

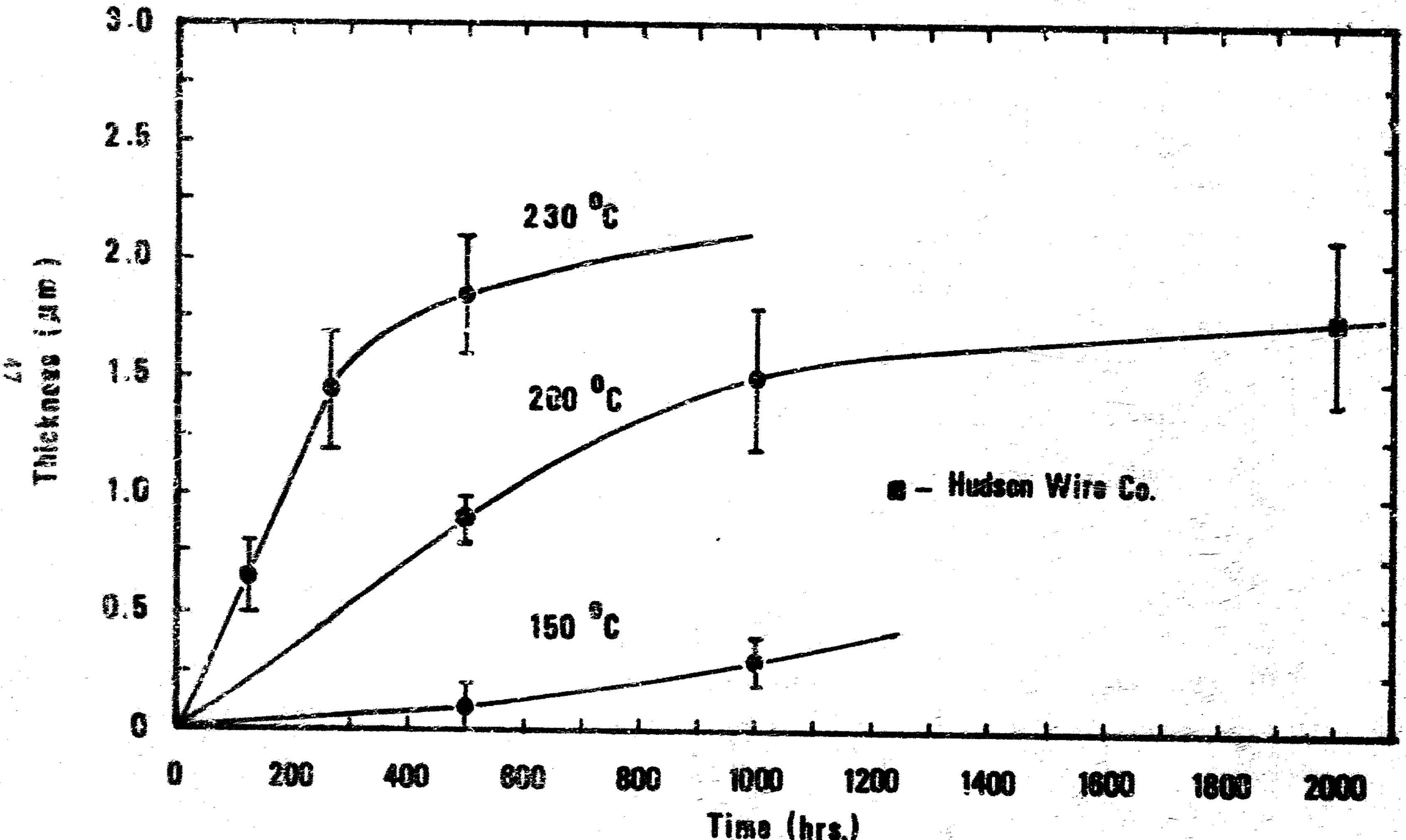


Figure 21. Thickness of cuprous oxide layer on No. 20 (19/32) Kapton insulated unilay wire as a function of time and temperature.